arXiv:cond-mat/9810351v2 [cond-mat.str-el] 10 Mar 1999

High frequency magneto-impedance of double perovskite $La_{1.2}Sr_{1.8}Mn_2O_7$: secondary transitions at high temperatures

P. V. Patanjali, P. Theule, Z. Zhai, N. Hakim, and S. Sridhar[a]
Physics Department, Northeastern University, 360 Huntington Avenue, Boston, MA 02115

R. Suryanarayanan, M. Apostu, G. Dhalenne, and A. Revcolevschi,
Laboratoire de Chimie des Solides, UA 446, Universitě Paris-Sud, 91405 Orsay, France

Radio frequency magneto-impedance measurements reveal a pronounced anomaly at $260K$ besides the main MI transition at $125K$ in the double perovskite material $La_{1.2}Sr_{1.8}Mn_2O_7$. This feature is not seen clearly in static resistivity and magnetization measurements. We suggest that this anomaly represents short-range magnetic correlations enhanced at radio frequencies, with the easy axis along the $c-$axis.

The observation of colossal magnetoresistance (CMR) in perovskite manganites $La_{1-x}A_xMnO_3$ ($A = Sr, Ca$) [113] has triggered further research into related systems [1–4]. The CMR in these materials is normally observed at temperatures close to the ferromagnetic-to-paramagnetic transition associated with a metal insulator (MI) transition. Following the double exchange mechanism of Zener [5], based upon the strong on-site (Hund's rule) coupling between the charge carriers (e_g-like state) and the local spins (t_{2g}-like state), several models [6–10] have been proposed to account for these properties, but many of the observed features cannot be accounted by the double exchange interaction alone. These well-studied 113 compounds can be considered as the $n = \infty$ members of the Ruddlesden-Popper (RP) series $(La_{1-x}Sr_x)_{n+1}Mn_nO_{3n+1}$ which can be described as intergrowths between $La_{1-x}Sr_xMnO_3$ perovskite blocks and rock-salt-type layers $(La, Sr)O$.

In order to examine further the relation between CMR, magnetic and MI transitions, attention has been focussed on other materials with reduced dimension n [11–14]. In particular, for the $n = 2$ member of the RP series $(La_{1-x}Sr_x)_{n+1}Mn_2O_7$(327), the material is antiferromagnetic for $x = 0$, while in the region $0.2 \leq x \leq 0.4$ the material is ferromagnetic and exhibits an MI transition at T_c. The maximum $T_c = 125K$ obtained in this series is for $x = 0.4$. Moritomo et al. [15] have reported a high value of CMR in $x = 0.4$ composition at temperatures near and far away from T_c.

Most of the experiments that probe the manganites are static in nature and have limited capabilities in elucidating the basic mechanisms involved. Recent dynamic measurements like EPR [16] and FMR [17] have provided microscopic evidence for the formation of Jahn-Teller polarons and spin wave resonance, respectively, in the manganites. In $La_{1-x}Sr_xMnO_3$, Srikanth et al. [18] have very recently observed additional new features in the rf impedance measurements, that are not clearly visible in the dc resistivity and magnetization measurements. These results show that the dynamic rf measurements reveal new transitions, and in addition also give information on the collective response of spin and charge dynamics. In this report we describe, for the first time, temperature and field dependence of radio frequency dynamic response of the double perovskite $La_{1.2}Sr_{1.8}Mn_2O_7$. We focus on a pronounced anomaly around $260K$ observed in many samples and suggest that this anomaly represents magnetic correlations, perhaps 2-D in nature, with a single energy and temperature scale.

Single crystals (5 cm long and 0.5 cm diameter) of $La_{1.2}Sr_{1.8}Mn_2O_7$ were grown from the melt by the floating-zone method using a mirror furnace [19]. Powder X-ray diffraction (XRD) analysis resulted in the lattice parameters $a = 3.864 \pm 0.002$ Å and $c = 20.130 \pm 0.006$ Å , in close agreement with those previously reported [15]. The polycrystalline material was synthesized by the conventional solid state sintering technique. No extra phases were detected by XRD and the lattice parameters were found to be identical to those determined in the case of the single crystals. Three single crystals labeled $SC1$, $SC2$ and $SC3$, and a polycyrstalline sample labeled PC were studied.

The rf measurements were carried out using an ultrastable tunnel diode oscillator. The sample is placed in a coil which forms the inductive part of the LC resonant circuit. In this technique, a change in the effective reactance X of the sample, caused by varying temperature, T magnetic field H, or angle θ (between crystalographic axis and H) leads to a change in the inductance of the coil which in turn results in a shift of the resonant frequency of the oscillator. The quantity that is measured is the change in the resonant frequency, $df(T) = [f_0(T_{\max}) - f(T_{\max})] - [f_0(T) - f(T)]$, where $f_0(T)$ is the empty coil frequency. From the elementary consideration of ac impedance and Maxwell's equations for magnetic, conducting materials, it can be shown that $df = -G(dX) \propto -d(\mu\rho)^{1/2}$. Where, $dX(T) = X(T_{\min}) - X(T)$ is the change in reactance, G the geometric factor and, $\rho(T, H)$ and $\mu(T, H)$ are the resistivity and permeability of the magnetic material, respectively. The change in the reactance is calculated using the above relation.

The stability of the circuit is very high, typically, $1Hz$

in $4MHz$ and the operating frequency is in the range $2-4MHz$ depending on the coil and sample used. The inductive coil with the sample is inserted into a Helium flow cryostat and coupled through a rigid coaxial cable, to enable temperature variation between $4.2K$ and $300K$. The magnetic field is applied by placing the sample coil-cryostat-assembly between the pole pieces of an electromagnet. The field dependent measurements were done with the field parallel to the $a-b$ plane ($H \,||\, ab$) and the $\hat{c}-axis$ ($H \,||\, c$), and the maximum field applied is $6KOe$.

The magnetization and CMR of the crystal have been described elsewhere [20]. Briefly, a sharp ferromagnetic to paramagnetic and metal - insulator (MI) transition is observed around $125K$, in the temperature dependence of magnetization, $M(T)$ and resistivity, $\rho(T)$ measurements, respectively. However, a strong deviation from the Curie-Weiss law was noted above $T > 200K$. Interestingly, in the case of sample $SC1$, while a very small change in slope is observed at around $260K$ in the $M(T)$, no such anomaly is observed in the $dc\ \rho(T)$ in both $ab-plane$ (ρ_{ab}) and $\hat{c}-axis$ (ρ_c) directions (inset, Fig. 2). From the field dependence of magnetization $M(H)$ at $5K$ it is found that the $easy-axis$ of magnetization lies in the $ab-plane$ which is in agreement with reported results [21,22]. The magnetic moment at $H = 5T$ was found to be $3.5\mu_B/Mn$ atom which is in close agreement with the theoretical value, $3.6\mu_B/Mn$ atom, ensuring the almost 100% spin polarization of the conduction electrons due to large Hund's-rule coupling energy [24].

Fig. 1 shows the shift in the radio frequency reactance, dX as the temperature is varied between $300K$ and $70K$, for single crystals $SC1, SC2$, and $SC3$. . As can be seen from the figure all the three single crystals show a sharp main transition at $T_c = 125K$. Results for the polycrystal sample PC (not shown) were similar but the transition at T_c was broadened. In the case of sample $SC1$ interestingly, a very strong jump, representative of a secondary transition, is observed at a temperature $260K$, which we call T^*. It is worth noting that the shift at this temperature is almost 35% of the shift at T_c and has similar characteristics as that of the transition at $T_c = 125K$. Such a transition is not seen in the static dc resistivity and is only observed as a very small change in slope in magnetization measurements. Samples $SC2$, $SC3$ and PC also show similar but weaker transitions around the same temperature. While the first transition at $125K$ is the well known MI transition (which is also observed in the $dc\ M(T)$ and $\rho(T)$ measurements), the origin of the transition at $T^* = 260K$ is quite intriguing and worth studying.

In the magnetization measurements, very weak features are observed in the vicinity of T^*, but are nowhere as pronounced as in Fig.1. In the literature similar weak features have been reported in double perovskite but have not been adequately addressed [15,22,23]. In the present ac measurements, the features are striking and unavoidable. In this paper we focus on this anomaly - a subsequent paper will discuss the details of the field and temperature dependence of the rf response over the entire temperature range. It is important to dwell on these unusual transitions as they may hold a key to an understanding of the basic mechanism involved in the CMR materials.

It has earlier been demonstrated from TEM (transmission electron microscopy) analysis that intergrowths could be present in these materials [25,22]. The intergrowths are missing or extra layers of SrO between MnO_6 octahedra, which could form higher order ($n > 2$) phases of RP series. The unit cell of 327 may be written as $SrO\,(La_{1-x}Sr_xMnO_3)_2$, where it is clear that MnO_6 octahedra are separated from each other by an insulating SrO layer. If the second transition is thought to be due to impurity 113 phase which forms due to missing of SrO layers, then this phase is likely to be $La_{0.6}Sr_{0.4}MnO_3$. The corresponding transition temperature of this phase is well above $300K$ [26]. Secondly, any phase transition in the MnO_3 sytem is, generally, associated with a large CMR at the transition. From the $\rho(T)$ it can be inferred that a large change in magnetoresistance is not observed at T^* even though as noted previously the overall magnetoresistance is substantial. Hence, the transition at T^* that we observe is not due to $La_{0.6}Sr_{0.4}MnO_3$ but due to some other mechanism. The transition at T^* could not be due to any other impurity phases since the experimental XRD [20]and electron diffraction [27] studies show that the sample is free from impurity phases. Therefore, one can rule out the intergrowths or impurities playing any role in inducing this transition.

In Fig. 2 we present the effect of external field in the $ab-plane$ ($H \,||\, ab$) and along the $\hat{c}-axis$ ($H \,||\, c$). As can be seen from the figure, in the case of $H \,||\, ab$ the change in dX at MI transition (at $125K$) decreases when compared to the same in the absence of field and, interestingly, the transition at T^* is almost smeared out. However, in the case of $H \,||\, c$ the change in dX at MI transition increases and, the transition at T^* disappears as in the case of $H \,||\, ab$. Since the easy axis of the magnetization is in the $ab-plane$ the decrease / increase in dX, in the case of $H \,||\, ab$ / $H \,||\, c$, can be understood in terms of decrease/increase in magnetization, respectively. If the T^* is due to an impurity phase (which ought to have an easy-axis in certain direction), as is expected from intergrowth mechanism, the dX at this temperature should have opposite responses for $H \,||\, ab$ and $H \,||\, c$ configurations, as in the case of MI transition. The present response, unequivocally, suggests that the transition at T^* is not due to impurity phases or intergrowths. It instead suggests some kind of ordering with a weak exchange interaction which gets destroyed in the presence of moderate magnetic fields.

Recently, Moritomo et al. [15] have observed a transition around $275K$ in $x = 0.4$ composition. However, no case has been made to explain it. In the case of $x = 0.3$ composition, Kimura et al. [21] observed a striking secondary MI transition in the $ab-plane$ (MI_{ab}) resistivity, in addition to the usual MI transition around $100K$

. They did not observe such secondary MI transition in the $c-axis$ resistivity measurements.. The result was ascribed to the $2D$ ferromagnetic correlations within the MnO_2 bilayers leading to MI_{ab} transition at $275K$. The $3D$ spin ordering across the nonmagnetic insulating $(La,Sr)O$ layers was suggested to be taking place at the $T_{c.}$ However, in the present crystal but for the magnitude change in the resistivities ρ_{ab} and ρ_c, no further difference is observed (inset, Fig. 2). In both the cases in the temperature range $T_c < T < T^*$ the sample shows insulating behavior.

The CMR, defined as $-(\rho(H)-\rho(0))/\rho(0)$, is almost 100% for $T_c < T < 150K$ and exceeds 10% in the entire temperature range. This CMR behavior is in sharp contrast with that of the $La_{1-x}A_xMnO_3$ perovskite, where it is present only below and close to T_c [1–4]. The enhanced CMR in the present compound could be due to anisotropic exchange interaction. The intra layer exchange interaction can be understood in terms of double exchange. Below T_c the interlayer coupling is established which contributes to the $3D$ magnetic ordering. The very large CMR observed in the vicinity of T_c, both below and above, is due to the alignment of the t_{2g} spins in the presence of applied magnetic field which reduces the scattering of the carriers by the local spins. The fact that large CMR is observed even above T_c indicates that some kind of spin correlation is maintained in this region. There could be many competing interactions/ordering above T_c such as antiferromagnetic superexchange, electron lattice (the Jahn-Teller effect) and charge ordering. From the inelastic neutron scattering study it has earlier been inferred, in the case of $x = 0.4$ double perovskite, that the spins in the neighboring layers are strongly canted [28] and that there exists in-plane antiferromagnetic (AF) correlations above T_c which lead to insulating behavior [29]. In the present crystals also from the inelastic neutron scattering study [30] it has been observed there is a coexistence of antiferromagnetism and ferromagnetism above T_c . Such a competition between ferromagnetic double exchange and antiferromagnetic super exchange has frequently been observed in the manganites which shows a large negative CMR at temperatures above T_c because of the field suppression of the AF fluctuations [31].

However, a careful analysis of the present results of $x = 0.4$ composition indicate that the transition at T* is not due to antiferromagnetic correlations but, probably, due to weak ferromagnetic correlations. The results show that main transition at T_c and the secondary transition at T^* are similar in nature.

In Fig. 3 the change in reactance, dX in the presence of $0.3T$ magnetic field, as a function of the angle between field and $\hat{c}-axis$ of the crystal at various temperatures is shown. The response at 10K can be considered purely magnetic since the field has no effect on ρ at this temperature (inset, Fig. 2). It can be seen that the overall response shows a reduction in permeability with the increase in the angle from 0^o to 90^o. Since the easy-axis of the 327 phase is in the ab-plane this reduction in μ is expected. However, at low angles one can see an increase in permeability which we identify as the response due to secondary phase. It is worth noting that the minima are separated by exactly 90^o. Therefore, it is not improper to conclude that the easy axis of the secondary phase is along $\hat{c}-axis$. This result coupled with the $dX(T)$ provides a strong evidence that the transition at T^* is ferromagnetic in nature and is independent of the ferromagnetic transition at T_c. Above T_c ($T = 188, 280$ and $300K$) it can be seen that a much reduced response (change in μ) persists. The reason for this small change is the existence of ferromagnetic fluctuations above T_c which is evidenced by the ferromagnetic hysteresis loop even at $295K$ [20]. The aforementioned field dependent anisotropy (Fig. 3) and temperature dependent (Figs. 1&2) measurements clearly suggest two kinds of ferromagnetic correlations occurring intrinsically.

It is very interesting to note that the neutron diffraction study by Mitchell et. al [32] shows a clear change in slope $d(a,b-axis)/dT$ at 260K in the a,b-axis vs temperature plot. However, they do not observe any change in $d(c-axis)/dT$ at 260K. Together, these two points clearly indicate that the T* is most probably associated with spin-lattice coupling and the associated ferromagnetic correlations lie in the ab-plane. Local lattice or Jahn-Teller distortions of the perovskite unit cells could lead to spin-lattice coupling. The coupling of the double exchange to the lattice degrees of freedom in manganites is theroreticallly studeid by Millis et al. [10] and Roder et al. [33] in terms of magnetoelastic polarons. The deviation from linearity in the temperature dependence of lattice parameters of $La_{0.6}Y_{0.07}Ca_{0.3}MnO_3$ [34] and $La_{0.65}Ca_{0.35}MnO_3$ [35] has, earlier, been interpreted in terms of a transition from large to small polarons. In the present case, the suggested 2D nature of the secondary transition indicates that it is probably a transition from large to small magnetoelastic polarons.

The present secondary transition is very important in understanding the microscopic picture of the manganites. Such intrinsic spin-lattice coupling can be sensitive to impurities in the crystal, which may be the reason for not observing T^* clearly in samples $SC2$ and $SC3$. It is worth mentioning that similar high frequency studies on very high quality single crystals of perovskite $YBa_2Cu_3O_7$ high temperature superconductor (HTS) gave rise to many novel features [36,37] which are not observed in general. In conclusion we have presented the temperature and field dependence of dynamic radio frequency permeability study of double perovskite, $La_{1.2}Sr_{1.8}Mn_2O_7$. These new results indicate a secondary transition at $260K$ similar to the main MI transition at $125K$. This anomalous secondary transition could be due to weak ferromagnetic correlations which are independent of the ferromagnetic ordering at T_c, which affect the dynamic permeability but are weakly coupled to charge transport.

We thank J.B.Sokoloff for useful comments. Work at Northeastern was supported by NSF-9711910 and NSF-9623720. This joint collaboration was supported by a US-France NSF-CNRS grant NSF-INT-9726801.

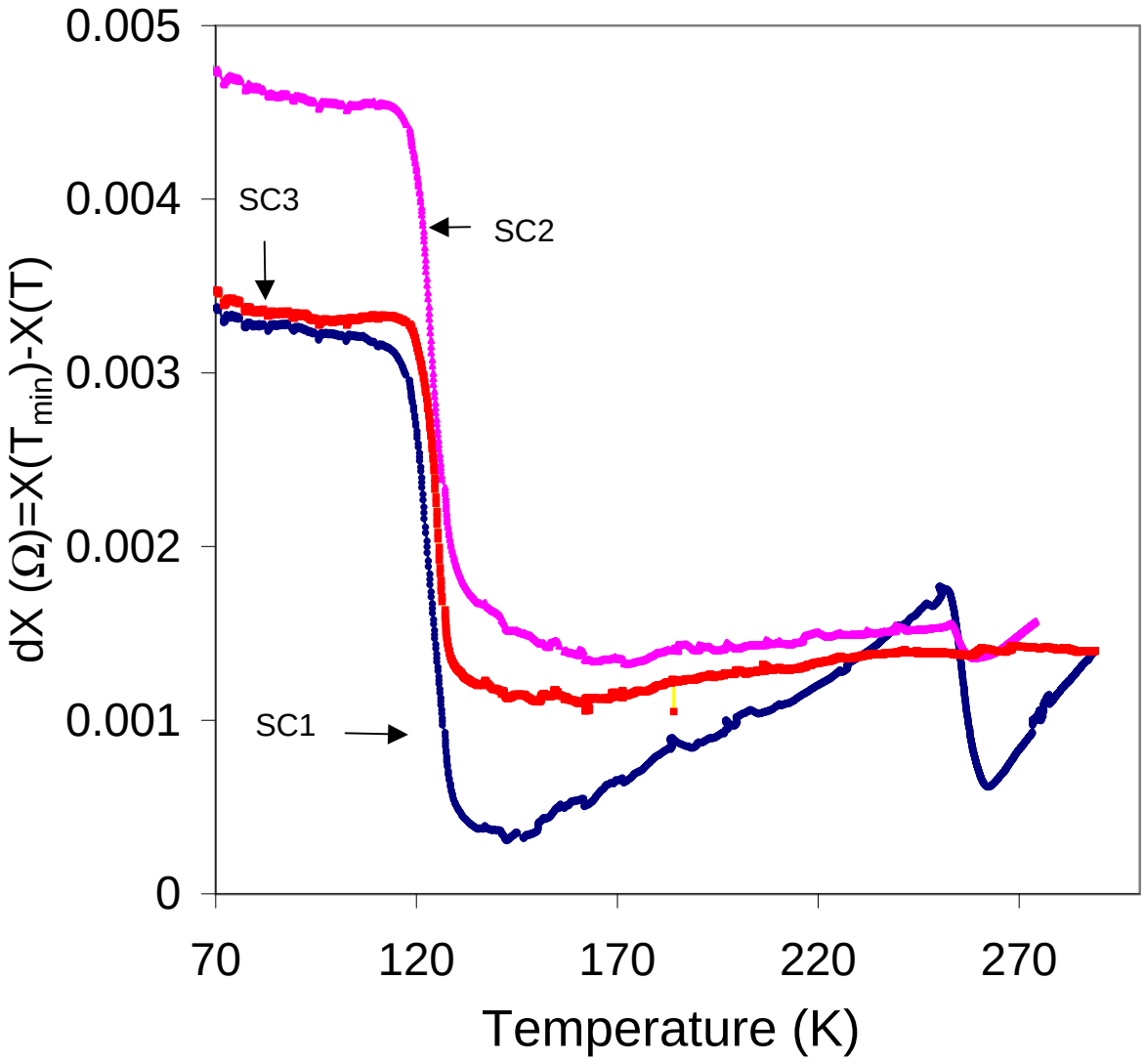
[a] electronic address : srinivas@neu.edu

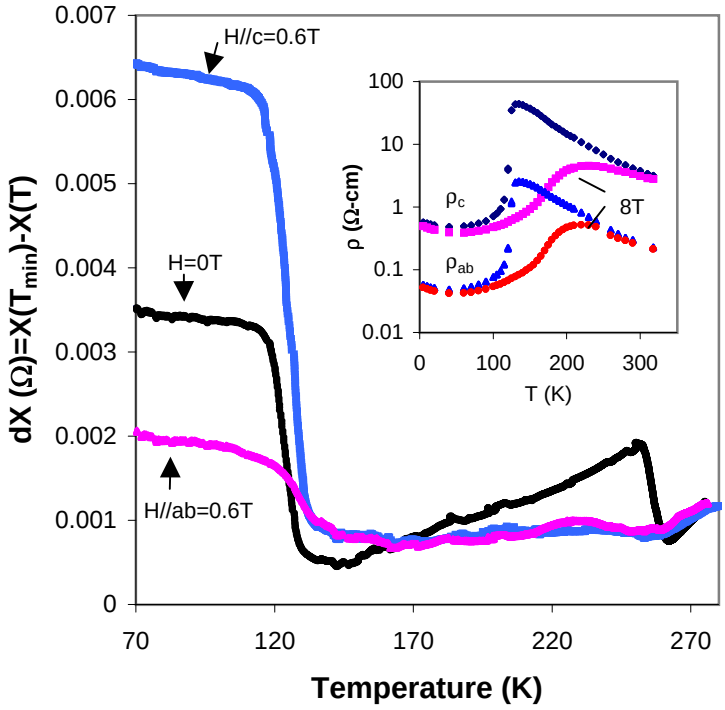
[1] R. von Helemolt et al., Phys. Rev. Lett., **71**, 2331 (1993).
[2] S. Jin et al., Science **264**, 413 (1994).
[3] C. N. R. Rao et al., Chem. Mater. **8,** 2421 (1996);
[4] A. P. Ramirez, J. Phys. Condens. Matter **9**, 8171 (1997).
[5] C. Zener, Phys. Rev., **82**, 403 (1951).
[6] P. W. Anderson and H. Hasegawa, Phys. Rev. **100**, 675 (1955)
[7] P.-G. de Gennes, Phys. Rev. **118**, 141 (1960)
[8] K. Kubo and N. Ohata, J. Phys.Soc. Jpn. **33**, 21 (1972)
[9] N. Furukawa, J. Phys.Soc. Jpn. **63**, 3214 (1994)
[10] A. J. Millis et al. Phys. Rev. Lett. **74**, 5144 (1995); Phys. Rev. Lett. **77**, 175 (1996); Phys. Rev **B 54**, 5389 (1996);Phys. Rev **B 54**, 5405 (1996).
[11] R. Mahesh et al., J. Solid State Chem. **122**, 448 (1996).
[12] P. D. Battle et al., J. Phys. Condens. Matter **8,** L427 (1996).
[13] P. Laffez et al., J. Appl. Phys. **80,** 5850 (1996).
[14] H. Asano et al., Appl. Phys. Lett., **70**, 2303 (1997).
[15] Y. Moritomo et al., Nature, **380**, 141 (1996).
[16] A. Shengelaya et al., Phys. Rev. Lett., **77,** 5296 (1996).
[17] S. E. Lofland et al., Phys. Rev. **B 52**, 15058 (1995).
[18] H. Srikanth et al., Science and Technology of Magneic Oxides, **494**, 311 (1998).
[19] A. Revcolevschi and R. Collongues, C.R. Acad. Sci., series **C, 266**, 1767 (1969).
[20] W. Prellier et al., Physica **B** , to be published.
[21] T. Kimura et al., Science, **274**, 1698 (1996).
[22] S. D. Bader et al., J. of Appl. Phys., **83**, 6385 (1998).
[23] Despina Louca et al., Phys. Rev. Lett., **80**, 3811 (1998).
[24] Y. Okimoto et al. Phys. Rev. Lett., **75**, 109 (1995).
[25] R. Seshadri et al., Chem. Mater., **9**, 1778 (1997).
[26] H. Kawano et al., Phys. Rev. **B 53**, R14709 (1996).
[27] M. Dechamps et al., unpublished.
[28] R. Osborn et al., Phys. Rev. Lett., **81**, 3964 (1998).
[29] T. G. Perring at al., Phys. Rev. Lett. (1997).
[30] T. Chatterji et al., unpublished.
[31] H. Kuwahara et al., Science **272**, 80 (1996).
[32] J. F. Mitchell, et al., Phys. Rev. B 55, 63 (1996).
[33] H. Roder et al., Phys. Rev. Lett., **76**, 1356 (1996).
[34] M. R. Ibarra et al., Phys. Rev. Lett., **75**, 3541 (1995).
[35] P. Dai et al., Phy. Rev. **B 54**, R3694 (1996).
[36] H. Srikanth et. al., Phys. Rev **B 55**, R14733 (1997).
[37] Z. Zhai et al., Physica **C 282-287**, 1601 (1997).

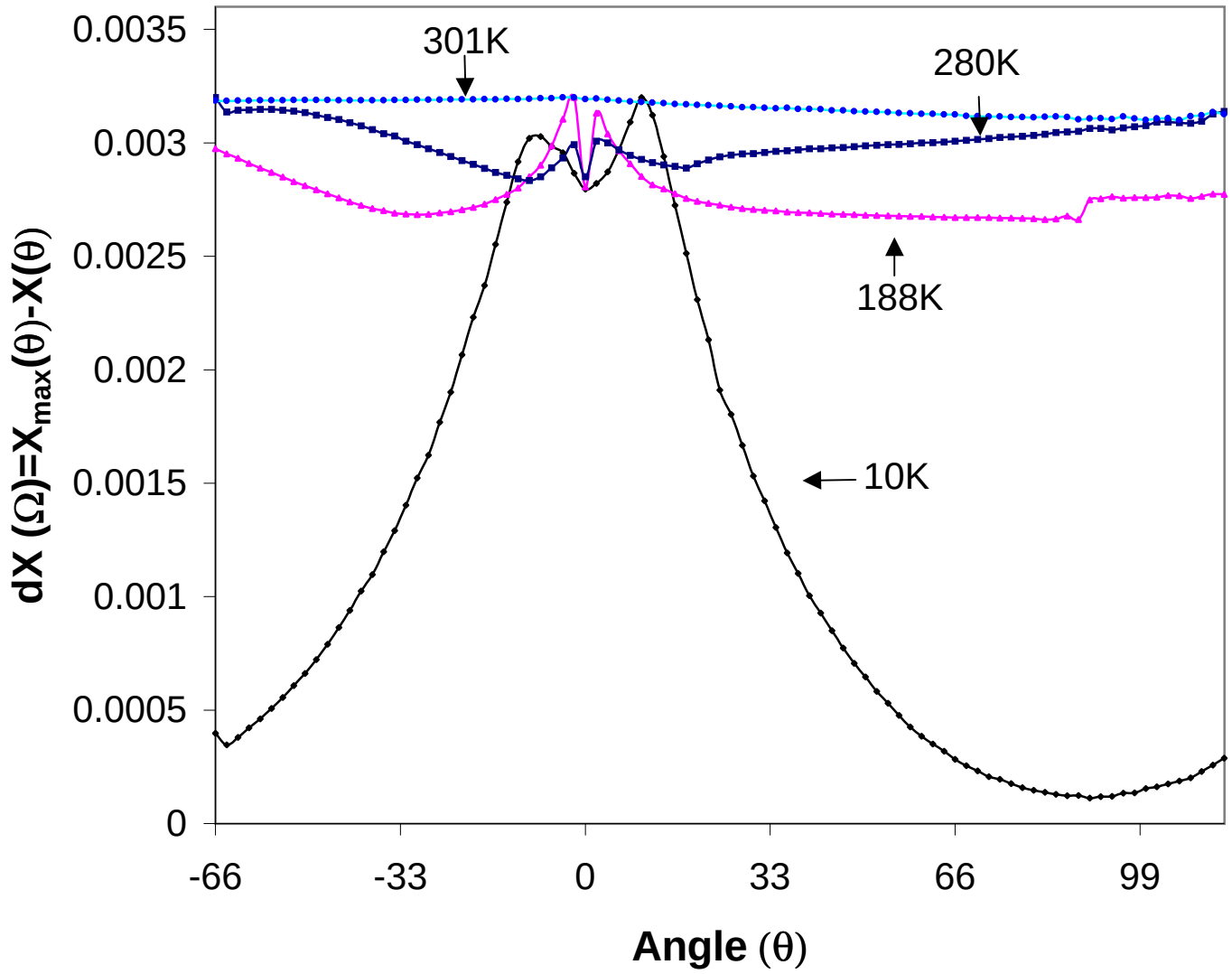
FIG. 1. Temperature dependence of radio frequency reactance for single crystals SC1, SC2 and SC3.

FIG. 2. Temperature dependence of rf reactance in the presence of magnetic field, H=0.6T for sample SC1. The change dX at T_c increases when the field is parallel to the c-axis contrary the change when the field is parallel to the ab-plane. Inset shows the temperature dependence of resistivity in the ab-plane and along c-axis, both in the presence and absence of field.

FIG. 3. Angular variation of rf reactance in the presence of $0.3T$ field at various temperatures for sample SC1. The minimun at 0° is representative of secondary transition while the minimum at 90° represents ferromagnetic ordering below T_c.


0.005
0.004
0.003
0.002
0.001
0
dX (Ω)=X(T_min)-X(T)
SC3
SC2
SC1
70
120
170
220
270
Temperature (K)


0.007
0.006
0.005
0.004
0.003
0.002
0.001
0
dX (Ω)=X(T_min)-X(T)
H//c=0.6T
H=0T
H//ab=0.6T
70
120
170
220
270
Temperature (K)
100
10
1
0.1
0.01
ρ (Ω-cm)
ρc
ρab
8T
0
100
200
300
T (K)


0.0035
0.003
0.0025
0.002
0.0015
0.001
0.0005
0
-66
-33
0
33
66
99
301K
280K
188K
10K
dX (Ω)=X_max(θ)-X(θ)
Angle (θ)